

Enthalpy of Vaporization of Organic Compounds at 25°C

V. Acetylacetone

R. J. IRVING* and INGEMAR WADSÖ

Thermochemistry Laboratory, University of Lund, Chemical Center, S-220 07 Lund 7, Sweden

The enthalpy of vaporization of acetylacetone has been measured calorimetrically at 25°C. ΔH_v (liquid, 81.4 % enol \rightarrow vapour, 93.3 % enol) = 41.8 ± 0.2 kJ/mole. $\Delta H_{v,e}$ (liquid, 100 % enol \rightarrow vapour, 100 % enol) = 43.2 kJ/mole.

Complexes of acetylacetone with metal ions cover a wide range of compounds but the study of the thermodynamic properties of these is hampered by lack of knowledge of the properties of acetylacetone itself. Published data on the vapour pressure of acetylacetone are meagre and not consistent: enthalpies of vaporization derived from these vary between 27 and 48 kJ/mole.¹ In this paper we describe experiments leading to the standard enthalpy of vaporization of acetylacetone at 25°.

EXPERIMENTAL

Acetylacetone (B. D. H. *puriss.*) was dried with Drierite and fractionated through a 10-plate column at atmospheric pressure until no impurities could be detected by gas chromatography. The temperature of the vapour at the top of the column (129°) suggested that almost pure enol form was distilling over but the distillate rapidly reverted to the equilibrium keto/enol mixture.

The water content was determined by gas chromatography using a Porapak column and found to be less than 0.03 %.

Part of the sample was used within two days of purification. This gave identical results with a sample which was stored for two months in glass ampoules at -20°C.

Calorimetric measurements. The calorimeter and the technique used have been described in detail elsewhere.^{2,3} The performance of the calorimeter was checked by measurements on a series of test substances (cyclohexane, octane, and decane) and the values obtained for the enthalpies of vaporization were, within limits of experimental error, in agreement with published values.² All measurements were performed isothermally at 25.00°.

* Chemistry Department, University of Surrey, Guildford, Surrey, England.

RESULTS AND DISCUSSION

The evaporation of acetylacetone is a rather complex process as it includes a tautomerization.

The keto-enol equilibrium in acetylacetone was originally determined by Meyer⁴ using the bromination technique which bears his name. There has long been a suspicion that this technique could disturb the equilibrium and within recent years several investigators have used NMR spectroscopy to determine this equilibrium. The best value for the liquid is believed to be 18.6 % keto, 81.4 % enol, quite close to Meyer's result⁵⁻⁷. The work of Briegleb and Strohmeier⁹ establishes the vapour at 25° as 93.3 % enol.

The enthalpy of enolization of acetylacetone vapour at 25° has been determined by an IR technique ($\Delta H = -10.0 \pm 0.8$ kJ/mole)⁸ and also from isothermal distillation measurements ($\Delta H = -9.2$ kJ/mole).⁹ The former value is used here. Several workers have used NMR methods to determine the enthalpy of enolization of the liquid.⁵⁻⁷ The best value is believed to be that of Reeves⁵ ($\Delta H = -11.3 \pm 0.4$ kJ/mole).

Interconversion between the keto and enol forms is slow in the gaseous phase but occurs readily in the liquid phase although by no means instantaneously.¹⁰ The equilibrium can therefore be disturbed by a comparatively rapid distillation process as there is an appreciable vapour pressure difference between the two tautomeric forms. Conant and Thompson¹⁰ used both barium hydroxide and sulphuric acid to catalyze the tautomerization. Even minute traces of barium hydroxide cause a slow yellowing of the acetylacetone due to a base-catalyzed decomposition and we abandoned this reagent as unsatisfactory.

Originally it was expected that the silver calorimeter itself would catalyze the interconversion so that there would be no accumulation of the less volatile component (keto) during the calorimetric process. However, in one series of measurements on pure acetylacetone a "warming-up" effect on the calorimeter was noticed after the vaporization was interrupted. As the keto \rightarrow enol reaction is known to be exothermic, this "warming-up" is what one would expect if there was a slow tautomerization reaction to re-establish the equilibrium mixture.

The procedure finally adopted was to add a trace of concentrated sulphuric acid to each sample immediately before the calorimetric experiment. Both the quantity of acid added, and the rate of evaporation was varied: no trend in the values was found a result of these variations in experimental procedure.

This leads us to believe that the liquid is always in keto/enol equilibrium, and, if this is so, the vapour pressure of the liquid and the composition of the vapour will also be constant, independent of the amount of liquid which has been vaporized.

With the present experimental technique there is a possibility that a true gas phase keto/enol equilibrium will not be attained in the calorimeter. For the extreme case with the same tautomeric composition in the gas phase as in the liquid phase (81.4 %) the experimental value would be 1.2 kJ/mole higher than the equilibrium value. However, quite apart from any tautomeric

rearrangement, the vapour in equilibrium with liquid acetylacetone will be richer in enol than the liquid, simply because of the higher vapour pressure of the enol. The enthalpy of enolization is small and minor deviations from equilibrium conditions will have a very small effect on the result (1 % deviation corresponds to 0.1 kJ/mole).

It appears therefore that conditions sufficiently close to true equilibria for the various interdependent gas/liquid, keto/enol processes have been attained and the experimental value will refer to the process at 25°

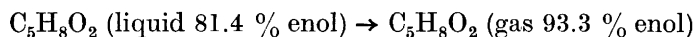


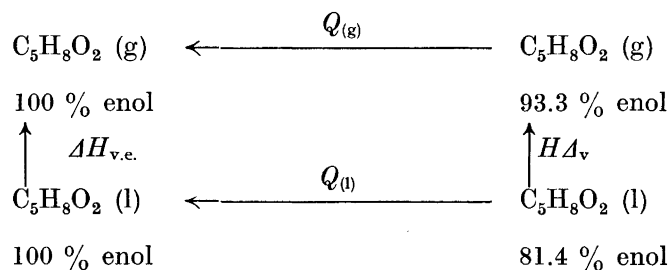
Table 1. Experimental enthalpies of vaporization, ΔH_v , for acetylacetone. Traces of concentrated H_2SO_4 added. Time for evaporation was in all cases close to 900 sec.

| Evaporated quantity, mg | ΔH_v , kJ/mole |
|-------------------------|------------------------|
| 115 | 41.84 |
| 115 | 41.78 |
| 116 | 41.75 |
| 116 | 41.76 |
| 116 | 41.91 |
| 116 | 41.80 |
| 114 | 41.71 |
| 146 | 41.64 |
| 87 | 41.74 |
| 87 | 41.73 |
| Mean | 41.77 ± 0.05 |

Results of the calorimeter measurements are summarized in Table 1. Twice the standard deviation of the mean is 0.05 kJ/mole but in order to account for possible systematic errors the result is given as 41.8 ± 0.2 kJ/mole.

Recently an indirect determination of the heat of vaporization from a consideration of the variation of vapour pressure with temperature led to the slightly lower value of 39.4 kJ/mole.¹¹

In the cycle is shown relationship between equilibrium keto/enol liquid and gas, and the pure enolic forms.

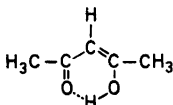


Using $\Delta H = -10.0$ kJ for the enthalpy of enolization of the vapour,⁸ and $\Delta H = -11.3$ for the enthalpy of enolization of the liquid,⁵ one obtains

$$Q_{(g)} = -0.67 \text{ kJ and } Q_{(l)} = -2.10 \text{ kJ/mole}$$

so the enthalpy of vaporization of 100 % enol liquid to 100 % enol gas $\Delta H_{v.e.} = +43.2$ kJ/mole.

The enolic form of acetylacetone exists as the hydrogen bonded ring



and one would thus expect little intermolecular hydrogen bonding. The boiling point for pure enol is unknown but is believed to be close to the distillation temperature (129°C) observed during the purification procedure. Using this value a ΔH_v /b.p. plot will give a point in a region characteristic for compounds not associated through hydrogen bonding.^{3,12}

Acknowledgements. This work has been supported by a grant from the *Swedish Natural Science Research Council*. The assistance of Mrs. Stina Bergström is gratefully acknowledged.

REFERENCES

1. Jones, M. M., Yow, B. J. and May, W. R. *Inorg. Chem.* **1** (1962) 166; Farrar, D. T. and Jones, M. M. *J. Phys. Chem.* **68** (1964) 1717.
2. Wadsö, I. *Acta Chem. Scand.* **20** (1966) 536.
3. Wadsö, I. *Acta Chem. Scand.* **22** (1968) 2438.
4. Meyer, K. *Ber.* **44** (1911) 1147.
5. Reeves, L. W. *Can. J. Chem.* **35** (1957) 1351.
6. Burdett, J. L. and Rogers, M. T. *J. Am. Chem. Soc.* **86** (1964) 2105.
7. Allen, G. and Dwek, R. A. *J. Chem. Soc.* **1966** 161.
8. Bernstein, H. J. and Powling, J. J. *J. Am. Chem. Soc.* **73** (1951) 4353.
9. Briegleb, G. and Strohmeier, W. *Angew. Chem.* **64** (1952) 409.
10. Conant, J. B. and Thompson, A. F. *J. Am. Chem. Soc.* **54** (1932) 4044.
11. Melia, I. P. and Merrifield, R. *J. Appl. Chem.* **19** (1969) 79.
12. Wadsö, I. *Acta Chem. Scand.* **23** (1969) 2061.

Received August 6, 1969.